A PERSONAL VIEW OF COAL SCIENCE: PAST, PRESENT AND FUTURE

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INTRODUCTION

Coal is our most abundant fossil fuel resource. Its major commercial use today is for electric power generation through combustion, and to a lesser extent as a feed for the manufacture of metallurgical coke. The potential uses for coal are broader, such as feeds for producing liquid fuels and chemicals; technologies are available, but are not economically competitive. New, more efficient and environmentally sound technologies for coal utilization will be required in the future, and these will arise from more detailed fundamental knowledge of coal structure and reactivity. What follows is a personal assessment of the state of the art in several areas of coal science, some critical opportunities for new chemistry in these areas, and some guesses about the impact such new information might have. Taken together, these suggested research areas could provide the scientific bases from which the required technologies of the future could emerge.

It should be noted that significant progress in basic understanding of coal structure and reactivity has been made in the last decade. In order to assess the extent of this progress, it is instructive to review what were considered to be key research needs at that time. In 1979 the writer and his colleagues detailed such needs (1), and in this paper they will be referred to as starting points for assessing current state of the art.

COAL CHARACTERIZATION

Today, as in the past (2,3), coal is thought of as a complex heterogeneous "organic rock", made up of fossilized remnants of primordial plant matter and incorporated inorganics. Coal is also a porous rock. Thus coals have organic, inorganic and physical structures. Because of the inherent heterogeneity of coals, and limitations in analytical instrumentation, systematic studies of these structures were limited in 1979. With the advancement of many modern characterization approaches, not available in 1979, clearer, more precise and in-depth knowledge of each of these structures has been attained, and understanding the ways in which they affect coal reactivity becomes possible.

ORGANIC STRUCTURE

Many average molecular models representative of the organic material in coals have been and continue to be proposed (4-8), and as expected, become more refined as new information is obtained. An excellent review of this area, published in 1981, is still relevant (9). These models are useful to guide thinking, but must be used with care, since they are average structures meant to represent functional group distributions and may not be completely accurate. All recent model structures may be viewed as "islands" of aromatic ring clusters, many of which contain substituents, held together by largely aliphatic, or aliphatic-heteroatomic "bridges". The relative sizes of the islands, bridges and substituents vary depending on rank.

About a decade ago, major unknowns of coal structure included the types and amounts of oxygen, nitrogen and sulfur functionalities, carbon aromaticities, the ring size distributions, and bridging structures for coals of different rank. Since then characterization techniques have been developed which allow much of this information to be obtained:

Organically bound oxygen functionalities (hydroxyl, carboxyl, and ethers by difference) may now be accurately determined by the O-alkylation method (10). This knowledge makes possible the understanding of the role of oxygen functionalities during coal reactivity. For example, the effect of hydroxyl group hydrogen bonding on the caking properties of bituminous coals has been demonstrated (11).

An X-Ray Photoelectron Spectroscopy (XPS) method has been developed to accurately speciate and quantify forms of organically bound nitrogen (12), including the basic pyridines and quinolines and the weakly acidic or neutral indoles and carbazoles. It is necessary to know how nitrogen is incorporated in the organic matrix, since it has been apparent for some time that nitrogen species play a role in coal asphaltene behavior (13) and in coal conversion chemistry (14).

Since 1979 major advances have been made in speciating and approximately quantifying forms of organically bound sulfur, involving reactive and direct measurements. The reactive method uses flash pyrolysis (15), while the direct measurements involve XPS (16) and X-ray Absorption Near Edge Structure Spectroscopy (XANES) (17, 18). The latter methods were applied to the suite Argonne Premium coals (19), and it was shown that aromatic sulfur forms increased directly with increasing rank of the coals studied (17). In addition these methods are now being used to follow the chemistry of organically bound sulfur under mild oxidation (20) and pyrolysis conditions (21).

Knowledge of ring size distributions has grown significantly in the last several years. In 1979, solid state 13C nuclear magnetic resonance (nmr) held real potential for this purpose, which has since been fulfilled. Aromatic ring cluster sizes have been estimated for the Argonne Premium coal samples based on some very elegant nmr experiments (22). For this sample suite varying from lignite to low volatile bituminous, the striking result is that the average ring cluster ranged between 9 (lignite) and 20 carbons (lvb), with most subbituminous and bituminous coals of this suite containing 14. This indicates an average size of 2-3 rings per cluster.

Another indicator of ring size distribution comes from coal depolymerization experiments (23). High levels of naphtha and distillate yields from a number of coals treated by this method indicate that average ring size distributions in the coals studied range from 1-3.

While methods are available today to get detailed information of the important coal structural features, they have not been uniformly applied to a standard suite of coals, and this represents an important research opportunity. Only the sulfur, nitrogen and nmr work described above have been done on the exact same suite of coals. This is necessary in order to get an idea of the parametric variations as a function of coal rank. Also, major opportunities now exist for using these methods to characterize starting and reacted coals and their products in order to be able to provide a basis for elucidating and understanding the detailed the chemistry taking place during conversion procedures.

INORGANIC STRUCTURE

Although the amounts of mineral matter in coals vary considerably, most contain about 10% (24). Mineral matter is inorganic material deposited before, during or after coalification of partially decayed biomass, and is largely in a reduced chemical state. Mineral matter is not necessarily inert during coal conversion processes, and has been reported to act beneficially in some cases as a catalyst for

gasification (25) and liquefaction (26) or detrimentally (27, 28). Therefore, a knowledge of the structures of the minerals present and their reactivities is important. Unfortunately, not much progress has been made in this type of characterization. Furthermore, the ways in which the inorganic matter is bound to the organic matter is not well understood. When coal is burned, the remaining inorganic mixture of oxides is called ash. Techniques to characterize the chemical compounds in ash, many of which are non-stoichiometric, are required. Sensitive probes to determine the compounds in which trace elements exist in native coals and in ash are being developed (29).

This information can impact on all forms of coal utilization including beneficiation, combustion, gasification, and liquefaction. For example, if mineral matter has catalytic effects during liquefaction, identification of the chemical species involved could lead to ways of enhancing its catalytic behavior. Better understanding of organic-inorganic interactions is needed to improve current coal cleaning procedures, and the determination of the compounds that make up slags found in furnaces might lead to ways of controlling the slagging phenomenon.

PHYSICAL STRUCTURE

The physical structure of coal has been described as a porous macromolecular gel (30). From the "porous rock" point of view, methods for determining surface areas and pore volumes on coals are needed. Depending on the coal, the adsorbing gas, the procedures used to acquire adsorption data and the equation used for the calculation, values of from 2-200 m2-g have been reported for the same sample (31). The difficulty in making these measurements is compounded because pore structures of subbituminous and lower rank coals collapse upon drying (32). Knowledge of surface areas and pore volumes are needed in order to help establish correlations between surface areas and chemical reactivity, particularly regarding access of gases and liquids to the interior of a coal particle.

From the "macromolecular network" point of view, much progress has been made in recent years in characterizing coals, and some reviews are available (33). It is well known that coals imbibe solvents, swell appreciably, and in some ways swollen coal networks take on elastomeric properties (35). Much work in recent years has focussed on adapting solvent swelling as applied to polymers to defining coal macromolecular structure in terms of Mc, the molecular weight between cross-links. There are many difficulties with translating polymer science techniques to coal (34), and the opportunities remain for finding reliable methods to determine Mc. This vital parameter could be used to follow the extent of coal network "depolymerization" during processing and for determining how many bonds need to be cleaved to reduce the "molecular weight" of coal from a solid macromolecular network to desired liquid products.

In recent years, another view of coal physical structure has been proposed (36), based on observed rapid and slow proton relaxation rates in nmr experiments. In this view, the macromolecular network is an "immobile phase" and is "host" to a number of many presumably smaller, mobile molecules, the "mobile phase", called by some "guests". As yet it has not been possible to distinguish between a long chain mobile molecule which exists independent of the network, and a similar molecule bound at a point to the network. Evidence to date suggests this model of unbound materials embedded in a rigid network may be valid for lignites and brown coals (37), but may not be for bituminous coals (38, 45). Regardless, this model has spawned some very important new work which addresses the true nature of

the bonding in coals.

If one assumes the host-guest, or two-phase model to be correct, then one would assume that a solvent or set of solvents could be found which would be able to dissolve large portions of the coal structure under mild solvent extraction conditions. Indeed recent reports suggest that N-methyl pyrrolidone (NMP) alone (39), or in combination with carbon disulfide (40) is capable of extracting up to 70% of some bituminous coals. The phenomenon is rank dependent, and appears to be most effective for low and medium volatile bituminous coals (40). Further understanding of this could help provide a basis for a low temperature procedure for obtaining liquid products from coals.

These observations, along with many others have called into question the nature of the bonding interactions in coals. It is fair to state that in 1979, most researchers believed that coal networks were held together almost entirely by covalent bonds, with minor contributions of ionic bonding in low rank coals (1). Perhaps the most important development in the last ten years and also the greatest opportunity for more research has been the realization that other bonding forms exist and exert major influences. The effect of aromatic-aromatic (pi-pi) interactions have been proposed and discussed (41, 42), as has charge transfer interactions (43). These interactions appear to contribute more and more to binding of coal structures as coals increase in rank and develop more aromaticity. Proton nmr relaxation experiments have differentiated between mobilities caused by heat and solvent swelling (44, 45) and confirm that non-covalent polar linkages become increasingly important with increasing rank. Computer modeling studies of proposed coal structures are consistent with this idea (46), and a qualitative representation of the types of bonding in coals as a function of rank has been proposed (47).

One important implication of this new understanding of how coals are held together is that it may be possible to convert solid coal into liquids using milder approaches than thermolysis, since these other interacting bonds are of much lower energy than covalent links. Use of milder conditions also has the potential of increasing the selectivity of the conversion of solid coal to lower molecular weight products, by avoiding the retrogressive reactions common to high temperature treatments. This area needs to be investigated further.

COAL LIQUEFACTION

Ten years ago, a number of coal hydroliquefaction processes were being developed, all based on a thermal conversion step, but differed in how hydrogen was provided: either from organic donors or molecular hydrogen, with or without catalysts (48), and these development programs were accompanied by relatively short-term laboratory research programs. During this same period, there were no process developments for pyrolysis and laboratory research was limited. Many of the hydroliquefaction process developments were completed by the mid 1980's, and provided the basis for substantial technological progress. For example, equipment performance was demonstrated on a large scale, and scale up issues were addressed. It was also demonstrated that coal liquids could be upgraded to transportation fuels using standard petroleum refining operations. Finally, successful methods of dealing with potentially harmful plant emissions were developed.

Major advances have since been made in the technology of coal hydroliquefaction in terms of

significantly increased yields of lighter, cleaner liquids, along with higher conversion selectivities and process efficiencies and costs. These improvements have come about largely by use of process staging and by having catalysts present in each stage. The scope of this progress has been reviewed in a recent U. S. Department of Energy needs assessment study (49). The current estimated cost of liquid transportation fuels produced from coal hydroliquefaction is in the range of US$ 35 per barrel (50).

It must also be mentioned that fundamental research also progressed during this period. Notable among the recent discoveries are the proposal of new mechanisms for hydrogen donation, involving solvent assisted processes (51), and new bond breaking chemistry, such as the use of water to cleave refractory diaryl ether covalent bonds (52). There is also new interest in pyrolysis as a result of the discovery that the catalyzed hydropyrolysis of bituminous coals can lead to liquid yields approaching 60% (53).

The study mentioned above lists many research opportunities in priority order, and the interested reader is referred to it for greater detail (49). In the writer's opinion, numerous research opportunities exist to gain understanding of the catalysis mechanisms involved in coal hydroliquefaction (54). For example, it is generally recognized that it may be relatively easy to affect the course of reactions after the primary products are out of the coal particle; by this time, however, the product distribution may already be determined (49). If a catalyst could be found which could influence the product distribution of the primary products as they are formed, entirely different types and quantities of products might be formed. Better understanding of catalysis mechanisms could lead to catalysts which use hydrogen more efficiently, and even to modification of naturally occurring mineral matter to improve its catalytic properties (26).

A more in depth understanding of the chemistry occurring as coal is heated to reaction temperature is a fertile area for new research (49). This would include the building of kinetic models containing intrinsic rate expressions for conversion of individual components, and include bond breaking, cross-linking, hydrogen donation, mass transport, and effects of solvents. This understanding can lead to methods to mitigate the retrogressive, i.e., molecular weight growth, reactions which are believed to take place at and even below presently used coal conversion temperatures. This might lead to pretreatment methods which would allow much lower temperatures to be used for the conversion process, presumably resulting in higher thermal efficiencies and greater selectivities to lighter products than now achievable. Finally, a coal structure-reactivity model needs to be developed, based on the coupling of the knowledge base of coal structure and kinetic models of its reactivity.

FUTURE OUTLOOK

By its nature, coal is a highly complex organic material, and many different approaches are required to gain the necessary scientific understanding. It is not at all certain that all of those have been mentioned in the above. In this context, the writer cannot help but remark that ten years ago the accomplishments of today's bio-science and technology, and specifically their application in coal science were not even thought of. Also, many environmental issues have not only surfaced, but been placed in the scientific and political forefront in the past ten years. To be applied, new science must have associated with it answers to any environmental concerns connected with it. Thus it is apparent that new research in coal science must be multi-disciplinary, including not only the familiar organic,

inorganic, physical and analytical chemistry, and chemical and mechanical engineering, but also solid state-condensed matter physics, geology, biology, and environmental science. No doubt, ten years from now, there will be others. As with recent advances in other fields involving complex materials, the greatest chance of success will come as a result of interactions among people specializing in these disciplines. The writer believes that the time for coal science to make major advances has arrived, and awaits the contributions of the scientific community.

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